

Spectroscopy of the Liquid Water Interface

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The molecular structure of liquid surfaces is a topic of much current interest. When a liquid forms an interface, the surface perturbation decays into the bulk with spatial variations on the molecular scale. Of particular interest is the molecular nature of the interface formed by liquid water in either air or vacuum, wherein the molecular density drops orders of magnitude. It has only become possible to study the molecular details of such interfaces in recent years. We report the results from novel studies of liquid water microjets by a variety of spectroscopic methods.

X-ray spectroscopy has proven to be a powerful means for probing the electronic structure of interfaces, but until now it has been prohibitive to apply this approach to volatile liquids. By employing the liquid microjet technology developed by Faubel and coworkers¹, we have been able to transcend these problems and study the water/vacuum interface under high vacuum conditions by EXAFS and NEXAFS techniques using the soft X-ray beamline 9.3.2 at the Lawrence Berkeley Laboratory Advanced Light Source.

The near edge structure observed at the oxygen K edge of water has been demonstrated to be a sensitive probe of the intermolecular environment of the bulk as well as the surface². Sharp fine structure observed in the near-edge region of water vapor has been assigned to a series of dipole transitions of the oxygen 1s(K) core electron to bound states just below the ionization potential. These NEXAFS states consist of a mixture of unoccupied molecular orbitals and Rydberg states. NEXAFS and EXAFS studies of 20 micron diameter liquid jets near the oxygen K-edge (539.7 eV) reveal a fine-structure pattern nearly identical to that found for isolated water monomers when the surface-selective (~5 angstroms) total ion yield (TIY) is measured. These measurements suggest that water molecules located in this interfacial region show significantly less perturbation due to intermolecular hydrogen bonds. In contrast, the total electron yield (TEY) shows a broadened and blue-shifted spectrum consistent with previous bulk-sensitive measurements of water multilayers.² Much effort has been directed to establish unambiguously that our TIY signal from the 20 micron jet arises from water molecules that are actually localized at the liquid surface, rather than isolated in the gas phase. Specifically, some of the higher energy Rydberg states, clearly exhibited in gas phase TIY spectra, are missing in our liquid microjet spectrum. In addition, the TIY from the liquid microjet exhibits weak EXAFS oscillations, consistent with a surface measurement. We have also conducted studies of smaller diameter microjets and observe more fine structure in the TEY spectra as the diameter of jet is decreased.

In addition, infrared spectra of the liquid microjets were taken at the Fourier Transform Infrared Microscope facility (bl. 1.4) at the Advanced Light Source. Infrared measurements made tangent to the microjet axis showed a strong feature at ~3600 cm⁻¹, characteristic of free (i.e. non hydrogen bonded) O-H stretching vibrations, while spectra measured at normal incidence closely resembled that of the bulk liquid. This sharp feature is indicative of an interface that is hydrogen terminated and is consistent with nonlinear optical measurements by Shen and coworkers³ for the liquid water/air interface. We have also measured the Raman spectrum of the liquid microjet, which closely resembles that of bulk liquid water.

The measurements presented here thus provide compelling new support for the existence of a hydrogen terminated liquid water surface predicted by computer simulations and experimentally demonstrated by Shen et al.³ Moreover, they support the predictions of Townsend and Rice⁴ that the water/vapor interface exhibits a hydrogen bonding network with coordination number significantly reduced from that of bulk water, actually tending towards a phase of isolated dimers. Evidently, thermal excitations produce a shell of very small water aggregates which then interact weakly, and subsequently disintegrate completely in forming the vapor phase. While this view is generally consistent with results of computer simulations, which reveal an interface wherein the average density drops to ca. 10% of the bulk value over a distance of 1-1.5 molecular diameters, the computed properties of such interfaces are extremely sensitive to the force field used, and clearly require more thorough study.

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² D. Coulman, et al., Chemical Physics Letters, 148(5) 371 (1988) and ref. therein

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⁴ R. M. Townsend and Stuart A. Rice, J. Chem. Phys., 94(3) 2207 (1991)